Speciation of Aluminum in Acidic Rivers of Nova Scotia Supporting Atlantic Salmon : A Methodological Evaluation

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SPECIATION OF ALUMINUM IN ACIDIC RIVERS OF NOVA SCOTIA SUPPORTING ATLANTIC SALMON: A METHODOLOGICAL EVALUATION

by

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ABSTRACT

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A method to separate the inorganic and organic forms of aqueous aluminum in freshwater using a fractionally loaded ion-exchange resin was assessed and modified to apply to acidic waters from Nova Scotia. The procedure was evaluated using synthetic and natural water solutions. Aluminum speciation was compared for Nova Scotia waters of diverse chemistries and during episodic increases in the acidity of some Atlantic salmon rivers. Organic (nonexchangeable) aluminum was the dominant form of aluminum (range 71-98%, mean 88%) and inorganic (exchangeable) aluminum was usually <50 µg/L in all waters sampled (ranges: pH 4.5-6.4, dissolved organic carbon 3-25 mg/L, total dissolved aluminum 7-422 µg/L). Total and organic aluminum concentrations were directly related to dissolved organic carbon content, and pH levels were inversely related to organic carbon, hence organic acids. Episodes of increased acidity associated with peak flows during autumn rainfall were related to increased concentrations of dissolved organic carbon. Total aluminum concentrations increased during these episodes and organic aluminum remained the dominant form. There was no increase of inorganic aluminum forms associated with decreases in pH level during the major hydrologic event of the year. Aluminum speciation in the salmon rivers of Nova Scotia thus differed from the established patterns for other regions where, during high flow periods, inorganic aluminum dominates and is a function of the pH level.

RÉSUMÉ

Lacroix, G. L., and K. T. Kan. 1986. Speciation of aluminum in acidic rivers of Nova Scotia supporting Atlantic salmon: a methodological evaluation. Can. Tech. Rep. Fish. Aquat. Sci. 1501: iii + 12 p.

Une méthode de séparer les formes inorganiques et organiques d'aluminium en solution aqueuse en eau douce avec une résine échangeuse d'ions fractionnairement chargée fut évaluée et modifiée pour être applicable aux eaux acides de la Nouvelle-Écosse. Des solutions synthétiques et des eaux naturelles furent utilisées pour évaluer ce procédé. La spéciation de l'aluminium dans des eaux de compositions chimiques variées ainsi que lors d'épisodes d'accroissement de l'acidité de quelques rivières à saumon atlantique en Nouvelle-Écosse fut comparée. L'aluminium non échangeable, donc de forme organique, était dominante (71-98% de l'aluminium, 88% en moyenne) et l'aluminium échangeable, donc de forme inorganique, était moindre que 50 µg/L dans tous les eaux échantillonées (écarts: pH 4,5-6,4; carbone organique dissous 3-25 mg/L; aluminium dissous total 7-422 µg/L). Les concentrations d'aluminium total et organique avaient un rapport direct aux taux de carbone organique dissous, et les niveaux de pH variaient en fonction inverse du carbone organique, donc des acides organiques. Durant les pluies d'automne, les épisodes d'accroissement de l'acidité aux périodes de crues étaient liés aux concentrations accrues de carbone organique. Les concentrations d'aluminium total augmentèrent durant ces épisodes et l'aluminium organique continua d'être la fraction dominante. Il n'y eut aucune augmentation des formes inorganiques d'aluminium ayant rapport aux décroîts du niveau de pH durant la crue. La spéciation de l'aluminium dans les rivières à saumon de la Nouvelle-Écosse diffère donc des modèles établis dans d'autre régions où, durant les périodes de crue, l'aluminium inorganique prédomine et varie en fonction du niveau de pH.

INTRODUCTION

Acidification of watersheds results in increased concentrations of aqueous aluminum in surface waters, temporally related to the mobilization of aluminum from a variety of sources and pools and its transport as affected by hydrological cycles and episodes (Cronan and Schofield 1979; Dickson 1980; Johnson et al. 1981; Campbell et al. 1984; LaZerte 1984; Seip et al. 1984; Driscoll et al. 1985; Hooper and Shoemaker 1985). The toxicological effects of the elevated concentration of aluminum that accompanies decreases in pH level in freshwaters depend on the biota present and the forms of aluminum that dominate (Freeman and Everhart 1971; Burrows 1977; Driscoll et al. 1980; Hall et al. 1985; Campbell and Stokes 1985; Neville 1985).

Increased concentrations of aluminum, mostly in the inorganic forms, are a major lethal factor implicated in the loss of salmonids and other fish species from acidified rivers in Scandinavia (Muniz and Leivestad 1980; Leivestad 1982; Rosseland and Skogheim 1984; Skogheim and Rosseland 1984; Skogheim et al. 1984). The toxicity of water chemistry to Atlantic salmon in acidic rivers of Nova Scotia has thus far been attributed to the effects of H^+ at low ambient calcium concentrations but the influence of high aluminum concentrations in these acidic rivers remains to be resolved (Lacroix 1985a, b; Lacroix et al. 1985). Knowledge of the relative concentrations of labile monomeric forms of aluminum and non-labile forms associated with fulvic and humic acids of natural origin is therefore necessary to evaluate water quality and the toxicology involved in the loss of salmon populations in rivers of Nova Scotia.

The purpose of this study was to select, evaluate, and modify if necessary a method appropriate for routine determinations of labile and non-labile forms of aluminum in freshwaters characteristic of the acidic salmon rivers of Nova Scotia. Having chosen a method, we quantified the forms of aluminum present spatially and temporally during the autumnal decline in pH levels noted after important precipitation events and increased flows. In the rivers studied, snowmelt is generally a less significant hydrological event than the autumn rainfall.

Various methods have recently been revised and used for the measurement and speciation of aluminum in acidic freshwaters (Driscoll 1980, 1984; Campbell et al. 1983; LaZerte 1984; Seip et al. 1984). The most appealing of these for our purpose was that of Campbell et al. (1983) which uses a fractionally loaded Chelex-100 ion-exchange resin to separate the exchangeable (labile inorganic, e.g. polymeric complexes, inorganic colloids) from nonexchangeable (non-labile organic, e.g. organometallic complexes, organic colloids) forms of aluminum. The method produces acceptable sample pH changes and does not significantly change the speciation of the aqueous aluminum. The differentiation between forms of aluminum on the basis of their respective rates of exchange with the resin is assumed to approximate that for the mechanism of toxic effects by adsorption on the gills of fish.

MATERIALS AND METHODS

The analytical procedure selected involved the physical and chemical separation of the following forms of aluminum: total filterable (dissolved) Al; nonexchangeable filterable (mostly organic) Al; and exchangeable filterable (mostly inorganic) Al.

All of the aluminum determinations were performed by graphite furnace atomic absorption spectroscopy (GFAA) using samples filtered through membranes of 0.45 µm porosity and prepared for analysis by addition of nitric acid (0.2%, vol/vol) to the filtrates. Determinations of total dissolved Al required only filtration of the sample and acidification of the filtrate, whereas determinations of nonexchangeable Al required prior treatment of the sample with an ion-exchange resin. Exchangeable Al was then calculated as the difference between total dissolved Al and nonexchangeable Al in a sample.

Campbell et al. (1983) used Chelex-100 ion-exchange resin to separate the forms of Al in natural water. They fractionally loaded the resin with Ca^{2+} and Mg^{2+} (1.0 mg Ca^{2+}/L; 0.5 mg Mg^{2+}/L; pH 5.0) to avoid the unacceptable pH changes that occurred when resin in the sodium or hydrogen form was added to water samples. We feel that their procedure of resin preparation is too tedious and not suitable for the preparation of a large batch of resin for routine aluminum speciation. After many trials we have come up with a relatively simple alternative method to prepare the ion-exchange resin.

Chelex-100 resin (100-200 mesh) supplied in the sodium form (Bio-Rad Laboratories) was first converted to the hydrogen form using 0.1 M HCl; 10 mL of the resin were then suspended in 1 L of deionized water; and 60 mL of a solution containing 0.065 M sodium acetate, 0.0125 M calcium acetate, and 0.01 M magnesium sulfate were added. After 20 min of stirring, the mixture was filtered and the resin rinsed thoroughly with a wash solution of pH 5.0 containing 3.0 mg/L Na, 1.0 mg/L Ca, and 0.50 mg/L Mg. The wash solution, prepared from NaCl, $CaCl_2$, and $MgSO_4$, had a composition (major ions) and pH level similar to the Nova Scotia waters of interest. The resin was resuspended in 1 L of the wash solution and the mixture was stirred for 10 min, at which time the pH of the mixture was between 5.8 and 6.0. After filtering the wash solution, the resin was treated with another 1 L batch of wash solution and the pH of the mixture decreased to 5.4-5.6. The resin was then recovered by filtration and stored at 4°C and 100% humidity until used. The purpose of the repeated batch treatment with the wash solution was to equilibrate the resin to a pH of 5.5 ± 0.1, and in most cases one or two such treatments were adequate.

The prepared resin was tested for its metal exchange capability and for the extent of resulting pH variations using a synthetic inorganic aluminum solution. The aluminum solution (100 ppb) was prepared by adding a stock potassium aluminum sulfate solution to a solution with an identical chemical composition as that of the wash solution

used in resin preparation. Resin (0.50 g) was added to 200 mL of the synthetic aluminum solution, the mixture was stirred for 1 h during which the pH of the solution was monitored, and aliquots of the sample were periodically filtered and analyzed. A synthetic aluminum solution blank without resin was also stirred for 1 h and analyzed.

After confirming the ability of the prepared Chelex-100 resin to exchange inorganic aluminum, the resin was applied to natural water samples. Resin (0.50 g) was added to water samples (200 mL) and, after 30 min of stirring, each sample was filtered and the filtrate was analyzed as for dissolved aluminum. The initial and final pH of the sample were also determined and duplicate tests were conducted on the initial batch of samples.

The above method of aluminum speciation involves the treatment of unpreserved samples as soon as possible after collection. Since it is preferable to do the resin exchange procedure in the laboratory rather than in the field, some aluminum will be lost if the sample is stored for a long period of time. To investigate the extent of aluminum loss in unpreserved samples, two samples were collected and one was filtered and then preserved (0.2% HNO_3, vol/vol) immediately in the field. Deionized water blanks were also prepared in similar manners to check for contamination.

The methodological assessment was done using water samples collected on a single date in November 1984 in five acidic streams of the Medway drainage in Nova Scotia (Fig. 1). Water samples were collected again in these and several other streams

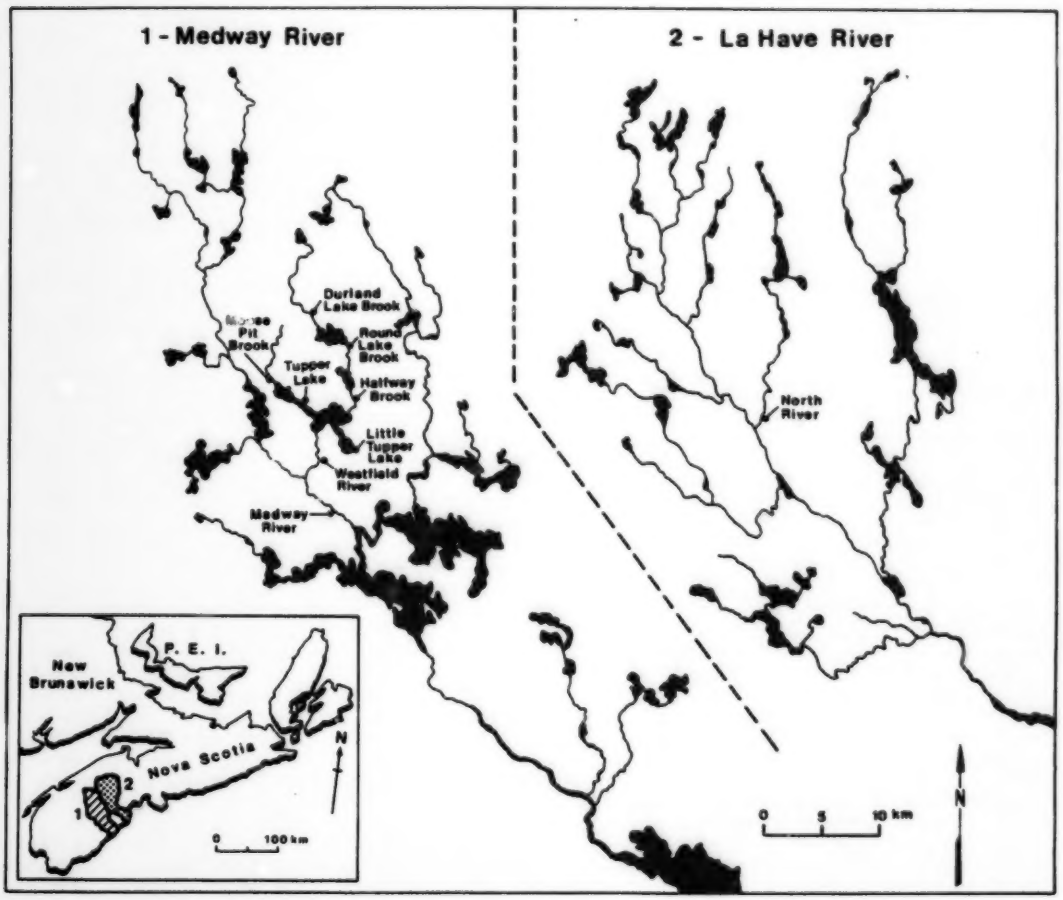

Fig. 1. Rivers and sites in Nova Scotia where samples for the speciation of aqueous aluminum were collected during 1984 and 1985.

(to cover a greater range of water quality parameters) in July and October 1985. To monitor episodic changes associated with autumn rainfall, samples were taken weekly in four streams between October 29 and December 21, 1985 (N=9). Samples were transported and kept at 4°C, and they were processed and analyzed for aluminum fractions within 48 h of collection.

Complementary analyses were performed, usually within 10 d, using standard methods (APHA et al. 1980). The pH level and Gran alkalinity (total inflection point, MOE 1980) were determined by electrometric titration. Metals (Na^+, K^+, Ca^{2+}, Mg^{2+}) were measured by flame atomic absorption spectroscopy and anions (Cl^-, SO_4^{2-}) by ion chromatography. Filtered (0.45 µm membrane porosity) and acidified (concd HCl, pH ≤2) samples were analyzed for dissolved organic carbon (DOC) content by the combustion-infrared method.

RESULTS AND DISCUSSION

METAL EXCHANGE CAPABILITY OF RESIN

Synthetic Aluminum Samples

Campbell et al. (1983) examined the effect of pH change on the exchange of monomeric hydroxyaluminum complexes with fractionally loaded Chelex-100 resin and found the rate of exchange of Al to be relatively constant over the pH range 3.3-5.0. They therefore deemed the measured pH changes ≤0.7 unit in 60 min to be acceptable. They also found that >85% of the Al is captured by the resin after 30 min (almost all after 60 min). Furthermore, in tests using synthetic Al solutions containing fulvic acid and humic acid, >97% of the Al remained in solution after a contact time of 30 min with the resin (Campbell et al. 1983). The optimal contact time is seemingly between 30 and 60 min, the timing thus offering a capability to separate inorganic Al and Al-fulvic/humic acid complexes.

The exchange of inorganic Al from the synthetic Al solution by the resin prepared by the new method was very rapid (98% absorption in 30 min) and the pH change of the sample was kept to a minimum (<0.2 pH units) (Table 1). The smaller pH change was desirable. We believe that sodium in the resin as well as in the samples plays an important role in maintaining the pH stability of the test solutions. The resin prepared by us was fractionally loaded with Na, Ca, and Mg, whereas that prepared by Campbell et al. (1983) was fractionally loaded only with Ca and Mg. Furthermore, on the basis of our exchange results (Table 1), we also suggest a contact time of 30 min with the resin; this was selected for the preparation of natural water samples.

Table 1. Concentrations of dissolved aluminum in a synthetic inorganic solution (100 ppb Al) over time during exchange with Chelex-100 resin (tests 1 and 2) and without treatment by resin (blank) and associated pH changes in the solutions.

Time (min)	Test 1 Al (ppb)	Test 1 pH	Test 2 Al (ppb)	Test 2 pH	Blank Al (ppb)	Blank pH
0	92	5.00	92	5.00	92	5.00
15	10	5.16	5	----	--	----
30	2	5.15	2	----	84	----
60	<1	5.18	<1	5.16	84	5.01

Nova Scotia Water Samples

Treatment of acidic water samples from some Nova Scotia salmon rivers with the resin resulted in very little exchange of Al (Table 2). Most of the

Table 2. Aluminum speciation by Chelex-100 resin (30 min), associated pH changes in samples, and dissolved organic carbon (DOC) concentration for water samples from several Nova Scotia rivers (28 November 1984).

	Dissolved aluminum (µg/L) Total	Non-labile[1]		Labile[2]	pH t=0	pH 30 min	DOC (mg/L)
Medway River	160	146	148 (92)	13	5.63	5.28	8.2
Westfield River	178	152	157 (87)	23	5.35	5.30	7.1
Halfway Brook	293	270	262 (91)	27	4.95	5.21	11.9
Round Lake Brook	328	298	296 (91)	31	4.94	5.21	12.1
Moose Pit Brook	256	246	243 (96)	11	4.83	5.12	15.0

[1]Nonexchangeable organic aluminum, duplicate determinations and average percent organic Al in parentheses.
[2]Exchangeable inorganic aluminum = total Al - non-labile Al.

dissolved Al (≥87%) remained in solution after 30 min contact with the resin indicating a dominance of nonexchangeable organic-Al forms in these waters. The pH changes in the samples were within ±0.4 units, which corresponds favorably to the pH changes encountered by Campbell et al. (1983). The precision of the duplicate tests was satisfactory (average coefficient of variation, C_v = 1.34%). The amount of exchangeable Al was probably low because of the high organic acid content of all samples; it was lowest in water samples with the highest DOC:Al (total) ratio (Table 2). The findings demonstrate the feasibility of applying Chelex-100 resin for aluminum speciation in the acidic salmon rivers of Nova Scotia.

Clair and Komadina (1984) conducted a preliminary evaluation of aluminum speciation in several rivers of Nova Scotia using the unmodified Chelex-100 procedure and found that no aluminum was removed from the water by the resin. They concluded that no labile (inorganic) Al fractions are present in these streams. However, the Al fraction measured after resin treatment was consistently higher (+130 ppb; 46.4%) than the total dissolved Al determinations, a difference they attributed to analytical precision lapses.

The validity of our ion-exchange procedure for separating labile from non-labile Al in acidic waters of Nova Scotia has more recently been verified using the dialysis procedure described by LaZerte (1984). Dialysis (using 1000 molecular weight cutoff membranes) of samples analyzed in this study indicated that 25-28% of dissolved Al was inorganic monomeric Al (D. G. Brewer and C. Armstrong, Department of Chemistry, University of New Brunswick, Fredericton, pers. comm.). However, because 1000-mwco tubing will permit entry of smaller fulvics and Al-fulvics within the time period required for equilibrium dialysis of the inorganic fraction (6-12%; LaZerte 1984), these results are probably an overestimation of the labile Al fraction. Our results using the ion-exchange method thus compare favorably with those using the dialysis method, given the expected limits (error) for highly colored, dilute waters where organic anions make up a substantial fraction of the total equivalents (LaZerte 1984).

Sample Preservation Considerations

Examination of the effect of sample storage confirmed the loss of dissolved Al (14%) in unpreserved versus preserved samples after long-term storage (60 d) (Table 3). Since samples treated with the ion-exchange resin must be unpreserved, a prolonged period of sample storage is unacceptable. Samples should be treated as soon as they are returned to the laboratory. The possibility of shorter term losses of Al (i.e. <48 h) and of changes in sample integrity during transportation should be determined in future studies. The changes in concentration of the synthetic inorganic Al solution that we measured within 30 min (Table 1, blank) seem to indicate that there is significant loss (9%) of labile Al, possibly due to polymeric molecules precipitating or adsorbing to the container walls. However, polymeric Al appears to usually be a minor component in natural waters (LaZerte 1984).

Table 3. Concentrations of dissolved aluminum in a water sample and deionized water blank filtered and preserved (0.2% HNO_3, vol/vol) in the field and in similar samples not filtered and unpreserved until analysis after 60 d storage.

	Dissolved aluminum (µg/L)	
	Filtered-preserved	Not filtered-unpreserved
Deionized water	1	<1
Westfield River	213	183

FIELD RESULTS

Spatial Differences in Aluminum Speciation

The Chelex-100 analytical method was applied to samples representing the spectrum of chemistry for acidic waters in southwestern Nova Scotia. Ranges for some parameters were: pH levels, 4.5-6.4; DOC, 2.7-24.6 mg/L; and total dissolved Al, 7-422 µg/L (Tables 2 and 4). Organic (nonexchangeable) Al was always the dominant form of aluminum (range 71-98%, mean 88%) and labile (exchangeable) Al was <50 µg/L in most waters sampled (Tables 2 and 4). In a study of aluminum speciation in lakes of the Laurentians of Quebec, Campbell et al. (1984) also found nonexchangeable Al to be dominant (range 51-100%, mean 71%) and, from photolysis results, concluded that the major portion of the nonexchangeable Al was associated with organic matter. A positive correlation between the concentrations of nonexchangeable Al and DOC provided further support of their conclusion. In each set of the Nova Scotia samples, DOC concentration and pH level were significantly correlated (-ve) and correlations of total Al and organic Al with DOC (+ve) and with pH (-ve) were usually significant (Table 5). Inorganic Al concentrations were independent of DOC concentration and were usually not well correlated with pH levels.

Temporal (Episodic) Changes in Aluminum Speciation

The forms of Al associated with the annual episode of decreasing pH levels during autumn rainfall were determined over a 2-mo period in four Nova Scotia streams of different pH levels. The streams, located in the same drainage system, also represent a continuum of ascending stream order (1-4): Moose Pit Brook, Halfway Brook, Westfield River, and Medway River (Fig. 1). In Moose Pit Brook, total Al decreased throughout autumn from >300 to <200 µg/L and organic Al was the dominant fraction (Fig. 2A). A slight rise in Al associated with the acid pulse and maximum DOC levels occurred during the second week of November but pH levels increased soon thereafter while DOC decreased markedly (by more than 50%) along with Al concentrations. Total and organic Al were both highly correlated with DOC (+ve) but there were no correlations between the forms of Al and pH or between DOC and pH (Table 6). However, the decrease in pH to <4.5 was apparently related to the initial

Table 4. Aluminum speciation by Chelex-100 resin, pH level, and dissolved organic carbon (DOC) concentration for water samples from Nova Scotia rivers and lakes (9 July 1985 and 29-31 October 1985).

	pH	DOC (mg/L)	Dissolved aluminum (µg/L)		
			Total	Labile[1]	Non-labile[2]
9 July 1985					
Little Tupper L.	6.21	2.7	23	2	21 (91)
North River	5.91	10.8	203	17	186 (92)
Medway River	5.34	11.5	222	20	202 (91)
Tupper Lake	5.31	8.8	199	19	180 (90)
Westfield River	5.05	11.2	275	54	221 (80)
Moose Pit Brook	4.77	22.8	277	5	272 (98)
Round Lake Brook	4.76	13.9	281	28	253 (90)
Halfway Brook	4.76	14.5	307	30	277 (90)
29-31 October 1985					
Little Tupper L.	6.37	4.6	7	2	5 (71)
North River	6.15	11.9	198	13	185 (93)
Tupper Lake	5.60	9.4	215	34	181 (84)
Medway River	5.58	11.3	186	10	176 (95)
Mersey River	5.46	6.9	119	34	85 (71)
Westfield River	5.34	10.2	206	22	184 (89)
Round Lake Brook	4.95	15.0	339	39	300 (88)
Halfway Brook	4.90	15.7	311	47	264 (85)
Moose Pit Brook	4.67	23.7	323	28	295 (91)
Durland L. Brook	4.52	24.6	422	49	373 (88)

[1]Exchangeable inorganic aluminum.
[2]Nonexchangeable organic aluminum and percent organic aluminum in parentheses.

Table 5. Pearson product moment correlations of aluminum species, pH level, and dissolved organic carbon (DOC) concentration for streams and lakes in Nova Scotia sampled in November 1984, July 1985, and October 1985.

	pH	DOC
28 November 1984 (N=5)		
Dissolved Al:		
Total	-0.87*	0.73
Organic	-0.89*	0.79
Inorganic	-0.30	-0.08
DOC	-0.88*	----
9 July 1985 (N=8)		
Dissolved Al:		
Total	-0.90**	0.79*
Organic	-0.90**	0.86**
Inorganic	-0.45	0.04
DOC	-0.78*	----
29-31 October 1985 (N=10)		
Dissolved Al:		
Total	-0.89***	0.90***
Organic	-0.86***	0.92***
Inorganic	-0.82**	0.58
DOC	-0.84**	----

*Significant at P<0.05.
**Significant at P<0.01.
***Significant at P<0.001.

Table 6. Pearson product moment correlations of aluminum species, pH level, and dissolved organic carbon (DOC) concentration for four Nova Scotia streams sampled during autumnal acidity episodes, 29 October-21 December 1985.

	pH	DOC
Medway River (N=9)		
Dissolved Al:		
Total	-0.96***	0.96***
Organic	-0.87**	0.92***
Inorganic	-0.72*	0.61
DOC	-0.94***	----
Westfield River (N=9)		
Dissolved Al:		
Total	-0.97***	0.90***
Organic	-0.93***	0.86**
Inorganic	-0.62	0.57
DOC	-0.94***	----
Halfway Brook (N=9)		
Dissolved Al:		
Total	-0.90***	0.75*
Organic	-0.98***	0.68*
Inorganic	0.42	-0.08
DOC	-0.67*	----
Moose Pit Brook (N=9)		
Dissolved Al:		
Total	-0.12	0.95***
Organic	-0.10	0.95***
Inorganic	-0.18	0.72*
DOC	-0.26	----

*Significant at P<0.05.
**Significant at P<0.01.
***Significant at P<0.001.

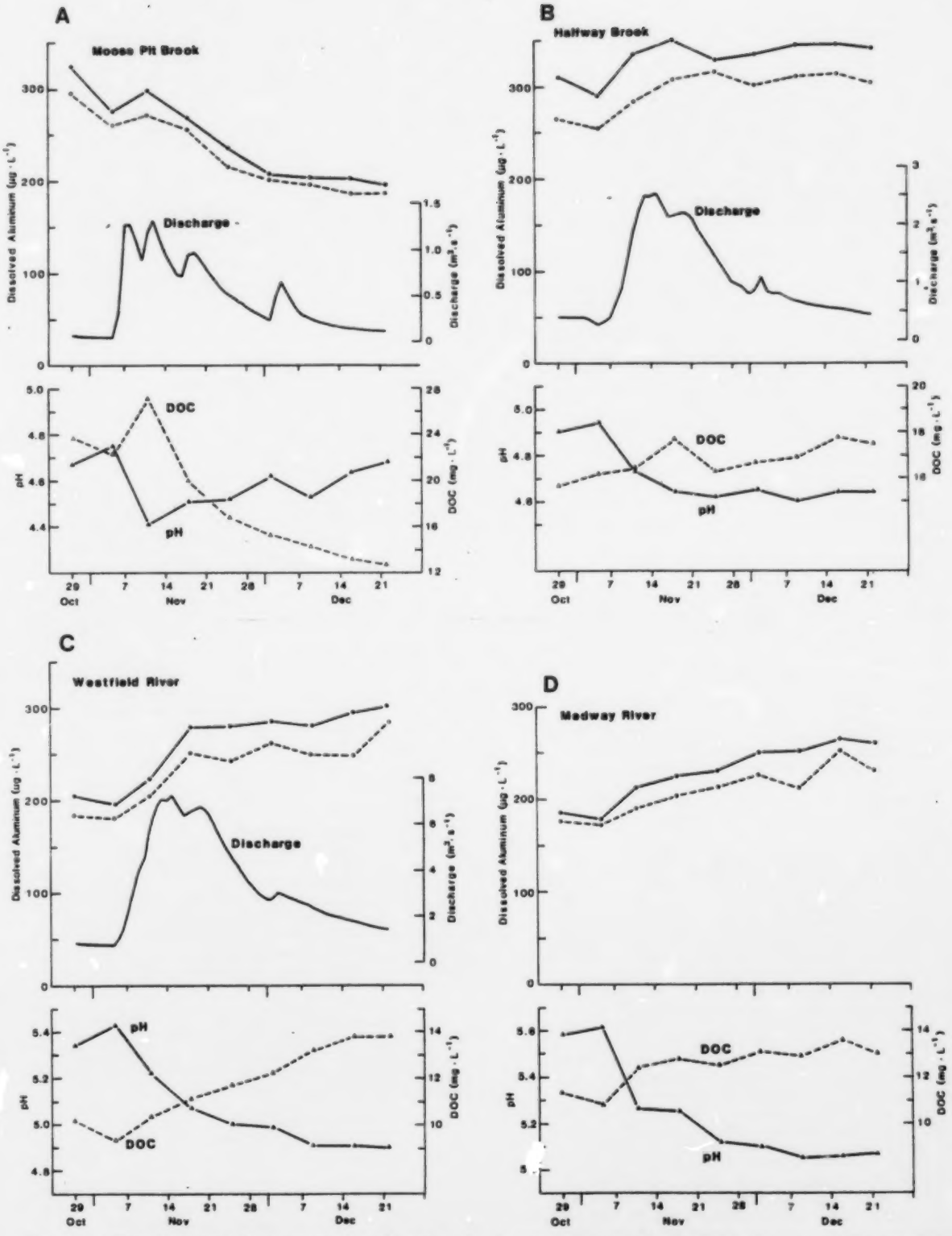

Fig. 2. Forms of dissolved aluminum (●—●, total Al; ○---○, organic Al), pH level (▲—▲), dissolved organic carbon (DOC) concentration (△---△), and mean daily flow (solid line) in (A) Moose Pit Brook, (B) Halfway Brook, (C) the Westfield River, and (D) the Medway River during autumn rainfall, 1985.

flushing with the increased flow of accumulated DOC in bogs and upper soil horizons (Fig. 2A). The DOC concentration then decreased rapidly in Moose Pit Brook because of its position as a first order stream and the pH level increased gradually back to initial levels. These indicate that the changes in pH were at least qualitatively related to the changes in DOC and that pH is to some extent controlled by organic (fulvic and humic) acids flushed during autumn episodes of precipitation. The gradual rise in pH after the DOC pulse may then be the result of dilution of organic acids by continued precipitation.

Trends in the other three streams differed from those in Moose Pit Brook (cf. Fig. 2A-D). The pH levels continued to decline or stayed at minimum levels throughout November and December, whereas DOC increased during the same period, the trend being inversely related to pH (-ve correlation significant in the Medway and Westfield rivers and Halfway Brook; Table 6). The slow and gradual rise in DOC following peak flows in these streams probably resulted from a lag in response time and the moderating influence of headwater lakes. Changes in pH mirrored those in DOC, indicating the importance of organic acids in controlling pH levels. The responses observed in these streams largely reflect their position in the watershed. Total Al and organic Al were highly correlated with pH (-ve) and DOC (+ve) (Table 6). Inorganic Al usually was not correlated to either because the changes in concentration were only minimal. Aluminum (total and dominant organic fraction) increased considerably with decreasing pH levels and rising DOC concentrations after the first week of November and remained at maximum levels throughout December (Fig. 2B-D). Inorganic Al was highest in Halfway Brook but concentrations were nevertheless usually <50 µg/L. Organic Al was dominant at all times and continuously high concentrations of DOC (>10 mg/L) in all four streams probably ensured against major changes in Al speciation regardless of changes in pH level that occur during autumn rainfall episodes. The close relationship between the concentrations of Al and DOC in all four streams indicates that inputs of Al are largely associated with the inputs of dissolved organic matter to the streams.

The importance of the organic complex of aluminum in colored, high DOC waters (Adirondack region of New York, Driscoll et al. 1980; Laurentians of Quebec, Campbell et al. 1984; Muskoka-Haliburton region of central Ontario, LaZerte 1984) is confirmed for the Nova Scotia streams. However, Driscoll et al. (1980) determined that inorganic monomeric aluminum increased dramatically with decreases in pH and was dominant during hydrologic events (late summer-autumn rainfall and spring snowmelt) but that organically complexed aluminum was generally predominant at other times. Similarly, LaZerte (1984) observed a switch from primarily organically complexed to inorganic monomeric aluminum during peak flows associated with spring snowmelt. Therefore, in both studies, the large fluctuations in total Al concentration were largely attributed to large fluctuations in the inorganic fraction of Al and controlled by pH changes in streams. Aluminum speciation in the Nova Scotia streams thus differed from the established pattern; there was no increase of inorganic aluminum during the major pH decrease and hydrologic event of the year associated with autumn rainfall and organic aluminum dominated all samples, accounting for increases in total aluminum and maximum concentrations. The inorganic Al dominance observed in the other regions during peak flows is a function of the large decrease in pH levels but probably also results because of the low concentrations of organic acids due to dilution by water from snowmelt during spring. Driscoll et al. (1980) reported minimum total organic carbon (TOC) concentrations (<5 mg/L) during snowmelt in the Adirondack region, and LaZerte and Dillon (1984) similarly found minimum concentrations of organic anions at that time in the central Ontario region. In Nova Scotia, the DOC concentrations in streams were almost always >10 mg/L and thus, probably in excess of that required to form organic complexes with most of the aluminum present at existing levels. Oliver et al. (1983) have determined that fulvic acid can complex 10 µmol of cations (average of carboxyl groups) per milligram of carbon (i.e. up to 260 µg Al per mg C).

In contrast with the above studies, Seip et al. (1984) found that the labile monomeric aluminum fraction (mainly inorganic complexes) almost always dominates in the relatively clear acidic streams in southern Norway. However, as in the other studies, the concentration of these inorganic species tends to increase with decreasing pH levels (autumn-spring sampling period). Schnitzer (1980) predicted, based on the decrease of the stability constant for the metal-fulvic acid complexes with decreasing pH, that a reduction in pH would result in a reduction of the degree of organic complexation of aluminum. Yet, Driscoll et al. (1980) found variations in organically chelated aluminum to be independent of pH but significantly correlated with total organic carbon (TOC) measurements in the 4-10 mg/L range. In our study, total and organic aluminum were significantly correlated with DOC in all four streams and with pH only in the three streams where DOC was <20 mg/L. There was no correlation of aluminum or DOC with pH in the headwater stream with the highest DOC concentrations (maximum, 27.1 mg/L). Fluctuations in total aluminum concentration in the Nova Scotia streams during peak flows are thus largely attributed to fluctuations in the organic (non-labile) fraction of aluminum in contrast to streams in the Adirondack region (Driscoll et al. 1980) and, in general, in central Ontario (LaZerte 1984). Both situations are found in central Ontario, although ordinarily the inorganic Al usually appears to dominate (B.D. LaZerte, Ontario Ministry of the Environment, Dorset, pers. comm.). The situation in streams of New England, where total aluminum peaks during high discharge and a positive correlation between total aluminum and organic anions exist (Haines and Akielaszek 1984), is probably very similar to that in Nova Scotia.

Our results provide further clarification of the toxicity to Atlantic salmon observed in acidic rivers of Nova Scotia (Lacroix 1985a; Lacroix et al. 1985), indicating that inorganic aluminum is not the lethal factor in these streams.

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Appendix 1. Water chemistry of Nova Scotia rivers and lakes sampled in 1984 and 1985 for aluminum speciation.

	pH	Concentration (mg/L) Na	K	Ca	Mg	Cl	SO_4	Alk[1]
28 November 1984								
Medway River	5.63	2.96	0.29	1.00	0.54	4.4	2.2	1.2
Westfield River	5.35	2.65	1.33	0.68	0.44	3.8	2.2	0.6
Halfway Brook	4.95	2.86	1.36	0.83	0.50	4.0	2.0	0.4
Round Lake Brook	4.94	2.74	0.42	0.81	0.47	3.8	1.9	0.4
Moose Pit Brook	4.83	3.28	0.28	1.16	0.71	5.1	1.7	0.2
9 July 1985								
Little Tupper L.	6.21	2.62	0.25	0.93	0.56	4.1	2.8	1.6
North River	5.91	2.41	0.23	1.30	0.47	3.4	2.4	1.9
Medway River	5.34	2.68	0.24	0.91	0.47	4.0	2.1	0.9
Tupper Lake	5.31	2.59	0.30	1.00	0.47	3.7	2.4	0.7
Westfield River	5.05	2.47	0.30	0.70	0.40	3.5	2.2	0.1
Moose Pit Brook	4.77	2.74	0.27	0.80	0.44	3.7	0.8	-0.2
Round Lake Brook	4.76	2.42	0.32	0.67	0.36	3.3	2.2	-0.3
Halfway Brook	4.76	2.45	0.28	0.66	0.36	3.3	1.9	-0.2
29-31 October 1985								
Little Tupper L.	6.37	2.61	0.28	0.86	0.59	4.3	2.9	1.8
North River	6.15	2.79	0.36	1.72	0.66	4.2	2.8	2.6
Tupper Lake	5.60	2.64	0.31	0.82	0.49	3.8	2.4	1.2
Medway River	5.58	2.91	0.29	0.96	0.52	4.2	2.3	1.2
Mersey River	5.46	2.99	0.26	0.75	0.47	4.7	2.7	0.7
Westfield River	5.34	2.62	0.32	0.69	0.44	3.6	2.2	0.9
Round Lake Brook	4.95	2.61	0.36	0.79	0.44	3.6	2.1	0.6
Halfway Brook	4.90	2.82	0.36	0.78	0.47	3.9	2.2	0.5
Moose Pit Brook	4.67	3.49	0.47	1.35	0.83	5.6	1.5	0.1
Durland L. Brook	4.52	3.19	0.67	1.05	0.61	5.4	1.4	-0.5

[1]Alkalinity, mg/L $CaCO_3$.

Appendix 2. Mean water chemistry of Nova Scotia rivers where samples were collected for aluminum speciation during autumnal acidity episodes, 29 October-21 December 1985.

	Medway River (N=9)	Westfield River (N=9)	Halfway Brook (N=9)	Moose Pit Brook (N=9)
pH	5.19	5.05	4.69	4.58
Alkalinity (mg/L $CaCO_3$)	0.97	0.53	-0.04	-0.48
Na^+ (mg/L)	3.10	2.76	2.85	3.03
K^+ "	0.33	0.35	0.38	0.39
Ca^{2+} "	1.06	0.79	0.83	1.02
Mg^{2+} "	0.59	0.49	0.50	0.65
Cl^- "	4.54	3.87	3.90	4.46
SO_4^{2-} "	2.47	2.31	2.38	2.37
DOC "	12.5	11.7	16.7	18.4
Dissolved Al (µg/L)				
Total	228	261	331	254
Labile[1]	21	27	37	15
Non-labile[2]	207	234	294	239

[1]Exchangeable inorganic aluminum.
[2]Noneachangeable organic aluminum.